The Effect of Strain on Thermodynamics of the Weakly First-Order Phase Transition

M.A.Fradkin[†]

Department of Mechanical and Aerospace Engineering

Carleton University, Ottawa, Ont. K1S 5B6, Canada

e-mail: `mfradkin@next.mrco.carleton.ca`

Abstract

Elastic matrix distortion around a growing inclusion of a new phase is analyzed and the associated contribution to the Gibbs free energy is considered. The constant-composition transformation from the parent to product phase is considered within the frame of Landau theory of phase transitions. The volume misfit between the inclusion and matrix is assumed to originate from the transformation volume change coupled with the phenomenological order parameter. The minimization of free energy with respect to the volume change and order parameter gives the dependence of Gibbs energy on the volume fraction of the product phase. The transformation proceeds in a finite temperature region with the equilibrium volume fraction dependent on temperature rather than at a fixed temperature as it would be expected for the first-order transition. The activation processes are shown to be irrelevant and the transformation kinetics is found to be fluctuationless.

05.70.Fh, 64.60.Qb, 64.70.Kb, 81.30.Hd

arXiv:mtrl-th/9508007v1 8 Aug 1995

Spontaneous strain is known to play an important role in many cases of the phase transformations in solids [1,2]. Due to the difference in crystalline structures and elastic properties of the co-existing phases the volume and shape misfits appear between the inclusion of the product phase and surrounding matrix of the parent one. An associated elastic strain both in the inclusion and in the matrix tends to relax this misfit by the cost of an additional elastic energy [3]. The minimization of this elastic energy defines the shape and crystallographic orientation of the new phase particles [4]. The elastic effects change qualitatively the phase diagram of heterophase systems and the phase rule is no longer valid since it does not take into account the elastic interaction between the phases which co-exist in a state of coherent equilibrium [5]. The 'chemical' free energy alone can not provide the equilibrium fractions of the phases with different composition through well-known double-tangent construction [6,7].

The elastic effects are considered in the present paper for the case of the first-order solid-state phase transition without change in a chemical composition. Such a transition may take place in pure elements, fixed-composition compounds and in alloys with very slow diffusion kinetics. The stresses are shown to result in a finite temperature interval of the phase co-existence with the equilibrium phase fractions depending on temperature whereas this co-existence appears at the single temperature point in the absence of elastic effects. The transition kinetics is shown to be changed as well and the activation processes does not control the transition development.

A usual approach [3] to elastic effects is to let the transformation proceed in the inclusion disconnected from the matrix, to let the 'zero-stress' transformation strain tensor to appear and than to bring the inclusion into an elastic contact with the surrounding matrix. The strain energy is then calculated using disconnected inclusion as an elastic reference state for the product phase. Though the new phase is sometimes considered to have different elastic moduli, calculations are mostly being done in the linear elasticity theory. However, when the transformation is sensitive to an applied external stress, a 'zero-stress' assumption is no longer valid and a non-linear dependence of the free energy of the new phase on the stress

level should be considered.

The simplest possible way to analyze the transition strain is to use Landau theory of phase transitions [8,9] taking into account the coupling of the phenomenological order parameter with the strain tensor components. Such a coupling has been recently considered for the case of a proper ferroelastic (martensitic) phase transition [10] and both the effect of hydrostatic and uni-axial pressure have been studied. In the present paper I consider the elastic interaction in a heterophase system for a model case of the spherical inclusions of the product phase embedded into an isotropic elastic matrix of the parent phase. The quadratic coupling of the order parameter with the volume change that corresponds to a variety of systems (e.g. see [11]) is analysed.

The remaining part of this paper is organized as follows. We begin with a linear elasticity analysis of the displacement field and the elastic energy associated with the volume change in an inclusion embedded into the isotropic matrix. Then the free energy difference between the infinite crystals of parent and product phases is considered within Landau theory and the coupling of the phenomenological order parameter with elastic strain is taken into account. The energy cost of the formation of a finite fraction of the new phase as inclusions inside the bulk crystal of the parent phase is than considered. After minimization of this free energy with respect to a volumetric strain, the resulting expression that depends on the volume fraction of the new phase is analyzed. Then the transformation kinetics is briefly discussed and the role of fluctuations is analyzed.

Let us start with the spherical inclusion in an isotropic matrix and consider the bulk crystal of the parent phase as a reference state for the elastic energy calculation. A spherical shape of the new phase inclusion presupposes either that transformation strain does not have shear components or that such components disappear upon averaging over the ensemble of twinned domains of the new phase composing the inclusion. The latter situation takes place in many cases of martensitic phase transformations in metals.

The radial displacement field $\mathbf{u}(r)$ appears due to the transformation and it has the following form determined by the elastic equilibrium conditions [12]

3

$$\mathbf{u}(r) = \begin{cases} a_1 r & \text{for} \quad r \le R \\ a_2 r + \frac{b_2}{r^2} & \text{for} \quad R < r \le R_0 \end{cases} .$$

Here R is the inclusion radius and $R_o = R/\sqrt[3]{\nu}$ is the radius of the spherical domain of the parent phase attributed to the inclusion for ν being the volume fraction of new phase. The first boundary condition states that the displacement field vanishes at R_o and the continuity of the displacement field across the interface implies the second boundary condition. Hence, one can get

$$a_1 = \frac{\epsilon_0}{3} , \quad a_2 = \frac{\epsilon_0}{3} \frac{\nu}{\nu - 1} \quad \text{and} \quad b_2 = \frac{\epsilon_0}{3} \frac{R^3}{1 - \nu} ,$$

where $\epsilon_0 = \mathrm{Tr}(\hat{\epsilon})$ is a volumetric strain inside the inclusion.

The elastic energy associated with the matrix strain and expressed per unit volume of the *new* phase is given by an expression

$$\Delta \mathcal{G}_{el}^{(m)} = \frac{K_0}{2} \epsilon_0^2 \frac{\nu + \gamma}{1 - \nu} ,$$

where $\gamma = (4\mu_0)/(3K_0)$ is the renormed ratio between the shear and bulk moduli of the parent phase. This energy corresponds to the stress that plays a role of the external pressure applied to the inclusion of the product phase.

The elastic energy (per unit volume of the new phase) associated with volumetric strain inside the inclusion is

$$\Delta \mathcal{G}_{el}^{(i)} = \frac{K_0}{2} \epsilon_0^2 .$$

Total elastic energy that has to be added to the Gibbs energy difference between the phases is equal to

$$\Delta \mathcal{G}_{el}(\epsilon_0) = \Delta \mathcal{G}_{el}^{(i)} + \Delta \mathcal{G}_{el}^{(m)}$$
$$= \frac{K_0}{2} \epsilon_0^2 \frac{1 + \gamma}{1 - \nu} . \tag{1}$$

This expression is valid for a sufficiently small ν when the inclusions of the product phase are well separated and the overlapping of associated spherical domains of the parent phase can be neglected.

The free energy difference between bulk crystals of the parent and product phases which are related by the symmetry breaking phase transition can be expanded in the mean-field Landau theory [8] in powers of the 'order parameter' η. The theory initially was developed for the second-order transition where η is continuous at the transition point, however, weakly-discontinuous first-order transitions can be considered as well [9]. If the symmetry groups of both parent and product phases are known *a priory* then the scalar order parameter can be used and the Ginzburg-Landau expansion of the free energy difference per unit of volume has the form [8,9]

$$\Delta\mathcal{G}_{\mathrm{GL}}(T,\eta) = \frac{\alpha}{2}(T - T_c)\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 \ .$$ (2)

where T_c is a critical temperature. Only the second-degree coefficient is supposed to depend on temperature and the equilibrium value of η is determined by the minimization of $\Delta\mathcal{G}$. Stability requires the highest order coefficient C to be positive and the third degree term $B \neq 0$ implies the first order of the transition.

Gibbs free energy (2) has two possible minima. One with $\eta = 0$ corresponds to a high-temperature undistorted phase stable for $T \geq T_c$. For

$$T \leq T_0 = T_c + \frac{1}{4}\frac{B^2}{\alpha C}$$

a low-symmetry phase exists with

$$\eta = -\frac{B}{2C}\left(1 + \left(\frac{T_0 - T}{T_0 - T_c}\right)^{\frac{1}{2}}\right).$$ (3)

The phase energies become equal at the temperature of the first-order transition $T_* = T_c + \frac{2}{9}\frac{B^2}{\alpha C}$ where the order parameter jumps from the $\eta = 0$ to

$$\eta = -\frac{2}{3}\frac{B}{C},$$

overcoming the activation energy barrier

$$\Delta\mathcal{G}_b = \frac{1}{324}\frac{B^4}{C^3}.$$

To analyze an associated strain effect the coupling of η with the strain tensor $\hat{\epsilon}$ has to be considered and the Ginzburg-Landau expansion should include the elastic terms (1). In the simplest case the symmetry allows the volumetric strain $\epsilon_0 = \text{Tr}(\hat{\epsilon})$ to be coupled with η in the lowest order by the following term:

$$\Delta \mathcal{G}_{int}(\epsilon_0, \eta) = D_0 \epsilon_0 \eta^2 \ . \tag{4}$$

Adding this term to the elastic energy (1) and finding the minimum of the resulting expression with respect to ϵ_0 we obtain the dependence of the volumetric strain inside the inclusion on the phenomenological order parameter in the form

$$\epsilon_0(\eta) = -\frac{D_0}{K_0} \eta^2 \frac{1-\nu}{1+\gamma} \tag{5}$$

This leads to a renormed Ginzburg-Landau expansion of $\Delta \mathcal{G}$ in powers of η [10]:

$$\begin{aligned}
\Delta \mathcal{G}(T, \eta) &= \Delta \mathcal{G}_{\text{GL}}(T, \eta) + \Delta \mathcal{G}_{el}(\epsilon_0(\eta)) + \Delta \mathcal{G}_{int}(\epsilon_0(\eta), \eta) \\
&= \frac{\alpha}{2}\left(T - T_c\right)\eta^2 + \frac{B}{3}\eta^3 \\
&\quad + \frac{C}{4}\eta^4\left(1 - \frac{2D_0^2}{K_0 C}\frac{1-\nu}{1+\gamma}\right) \ .
\end{aligned} \tag{6}$$

We have considered the unstrained parent phase as a reference state for an energy calculations, thus, the energy cost for the formation of the new phase (6) should be multiplied by its volume fraction. Choosing the case of $B < 0$ which implies a positive η in the product phase, we can write the expansion of total free energy per unit *system* volume in the following form

$$\begin{aligned}
\Delta \tilde{\mathcal{G}} &= \frac{C^3}{B^4}\Delta \mathcal{G} \\
&= \nu\left(\frac{\tau}{2}\zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4}\left(1 - \frac{\psi(1-\nu)}{1+\gamma}\right)\right) \ ,
\end{aligned} \tag{7}$$

with

$$\eta = -\frac{B}{C}\zeta \ , \quad \tau = \frac{\alpha C}{B^2}\left(T - T_c\right) \ \text{and} \ \psi = \frac{2D_0^2}{K_0 C} \ .$$

The dependence of $\Delta \tilde{\mathcal{G}}$ on ζ and ν is shown in Fig.1 for some τ, ψ and γ.

The state of equilibrium is determined by the minimum of this free energy with respect to both ζ and ν

$$\frac{\partial \Delta \tilde{\mathcal{G}}}{\partial \zeta} = 0 \qquad \text{and} \qquad \frac{\partial \Delta \tilde{\mathcal{G}}}{\partial \nu} = 0 \tag{8a}$$

$$\frac{\partial^2 \Delta \tilde{\mathcal{G}}}{\partial^2 \zeta} + \frac{\partial^2 \Delta \tilde{\mathcal{G}}}{\partial^2 \nu} > 0 \tag{8b}$$

$$\frac{\partial^2 \Delta \tilde{\mathcal{G}}}{\partial^2 \zeta} \frac{\partial^2 \Delta \tilde{\mathcal{G}}}{\partial^2 \nu} - \left(\frac{\partial^2 \Delta \tilde{\mathcal{G}}}{\partial \nu \partial \zeta} \right)^2 > 0 \ . \tag{8c}$$

Solving coupled equations (8a) we obtain

$$\zeta = \frac{2}{3} \left(1 + \frac{\psi}{1 + \gamma - \psi} \right) \tag{9}$$

$$\nu = \frac{1 + \gamma - \psi}{2\,\psi} - \frac{9\,(1 + \gamma - \psi)^2\,\tau}{4\,(1 + \gamma)\,\psi} \ . \tag{10}$$

The stability conditions (8b) and (8c) are satisfied for these ζ and ν if

$$\tau < \tau_* = \frac{2}{9} \left(1 + \frac{\psi}{1 + \gamma - \psi} \right) \ . \tag{11}$$

In the $\psi \to 0$ limit τ_* corresponds to the temperature of the first-order phase transition T_* in the absence of stresses. An important difference is, however, that now the product phase does not correspond to the free energy minimum above this temperature and, therefore, is *mechanically* unstable. The energy dependence on ζ is shown in Fig.2 for $\tau < \tau_*$. There is an activation barrier separating the initial $\zeta = 0$ state and the product phase that corresponds to minimum of free energy for $\zeta \neq 0$. However, there is no barrier in the free energy dependence on ν shown in Fig.3. It means that there exists a transformation path in the (ζ, ν) phase space that does not involve any activation process.

The classical phase rule allows the equilibrium co-existence of the parent and product phases of the same composition only at the fixed temperature T_*. However, the phase rule is based on the assumption that there is no elastic interaction between the phases. The finite equilibrium volume fraction of the second phase ν that corresponds to the minimal $\Delta \tilde{\mathcal{G}}$ in the present model appears in some temperature interval below τ_* and depends linearly on the dimensionless temperature τ according to Eq.(10) which is illustrated in Fig.4. The

system has to be cooled further down for the increase in ν, i.e. for the transformation to proceed.

The present model corresponds to the 'athermal' kind of martensitic transformation in metals when the transformation begins at some start temperature M_s, but the parent phase still exists until the temperature goes down to M_f, a martensite finish point. The finish point M_f corresponds to $\nu = 1$ and the present model can not be used in this region because the inclusions of the new phase are supposed to be well separated.

In the absence of stresses the transformation rate is determined by Arrenius factor for the activation energy barrier as well as by the nucleation and growth kinetics. The system can be supercooled and the transformation proceeds with a finite rate at any constant temperature below T_* and can be completed at the same temperature in a finite time. In the present model the transformation does not involve any (thermal) activation process as there is no energy barrier. It means that fluctuations do not play an important role, supercooling is impossible and there is no Arrenius factor in the transformation rate which therefore should be very high. Such a 'non-activated' kinetics is a characteristic feature of the martensitic transformations. If the temperature interval between M_s and M_f is narrow enough than for any real cooling rate transformation would be completed almost instantly. This is known to be the case for so-called 'isothermal' kind of martensitic transformations in metallic alloys.

To conclude we have analyzed an effect of elastic stresses in the matrix on the thermodynamics and kinetics of the first-order phase transformation in an embedded inclusion. The coupling of strain with the transformation degrees of freedom has been considered in the frame of Landau theory of phase transitions. The transition takes place in some temperature interval rather then at a certain temperature and the transformation kinetics appears to be activationless. This model may describe martensitic transformations in some metallic alloys.

ACKNOWLEDGMENTS

REFERENCES

[†] On leave from the Institute of Crystallography, Russian Academy of Sciences, Moscow, 117333, Russia

[1] J.W. Christian, *Theory of Transformations in Metals and Alloys*, Pergamon, Oxford, 1965.

[2] A.G. Khachaturyan, *Theory of Structural Transformations in Solids*, Wiley, New York, 1983.

[3] J.D. Eshelby, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull, Vol.3, (Academic Press, New York, 1958), p.79.

[4] A.L. Roitburd, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz and D. Turnbull, Vol.33, (Academic Press, New York, 1978), p.317.

[5] J.W. Cahn and F. Larche, Acta Metall. **30**, 51 (1982).

[6] J.W. Cahn and F. Larche, Acta Metall. **32**, 1915 (1984).

[7] W.C. Johnson and P.W. Voorees, Metall. Trans. **18A**, 1213 (1987).

[8] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd edition, Oxford, Pergamon, 1981.

[9] J.C. Toledano and P. Toledano, *The Landau theory of phase transitions*, World Scientific, Singapore, 1987.

[10] M.A. Fradkin, Phys. Rev. B **50**, 16326 (1994).

[11] M.A.Fradkin, *On thermoelastic phenomena around orientational ordering transition in crystalline C_{60}*, preprint #9503023 in E-print archive at `cond-mat@xxx.lanl.gov`, *Phys. Rev. Lett.*, submitted

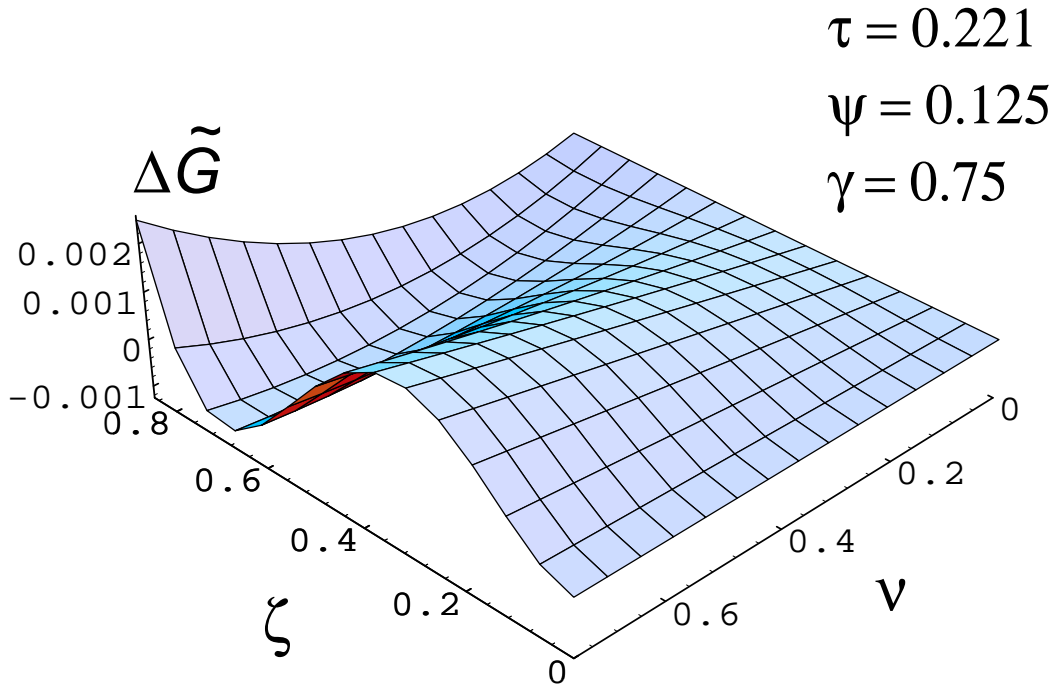[12] L.D. Landau and E.M. Lifshitz, *Theory of Elasticity*, 3rd edition, Oxford, Pergamon, 1981.

$$\tau = 0.221$$
$$\psi = 0.125$$
$$\gamma = 0.75$$

FIG. 1. Dependence of $\Delta\tilde{\mathcal{G}}$ on the order parameter ζ and the volume fraction of the new phase ν.
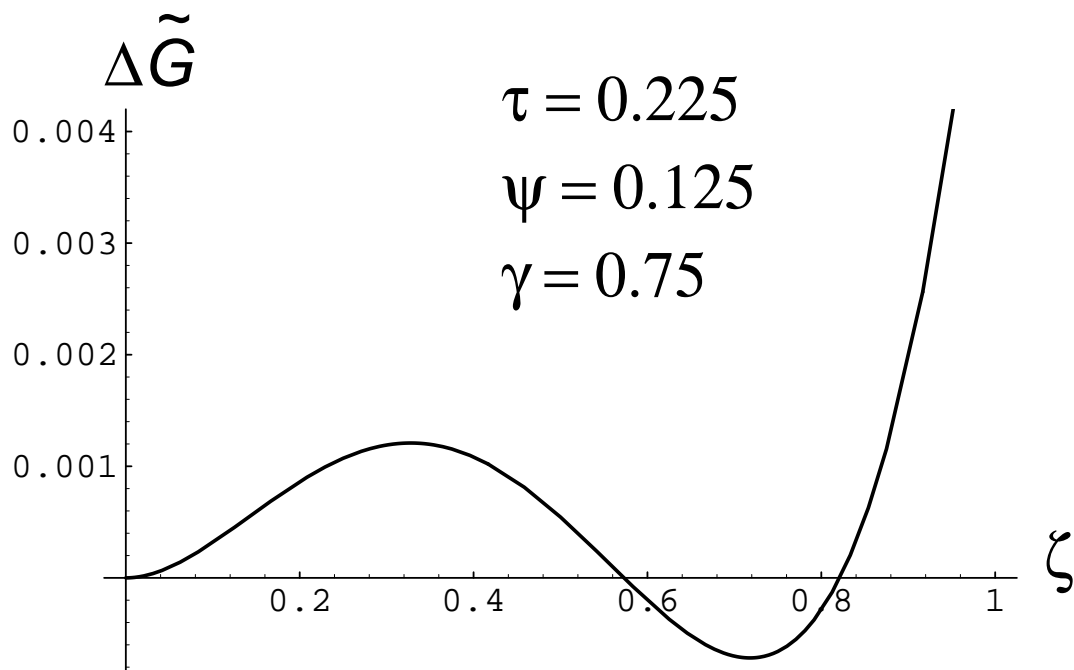
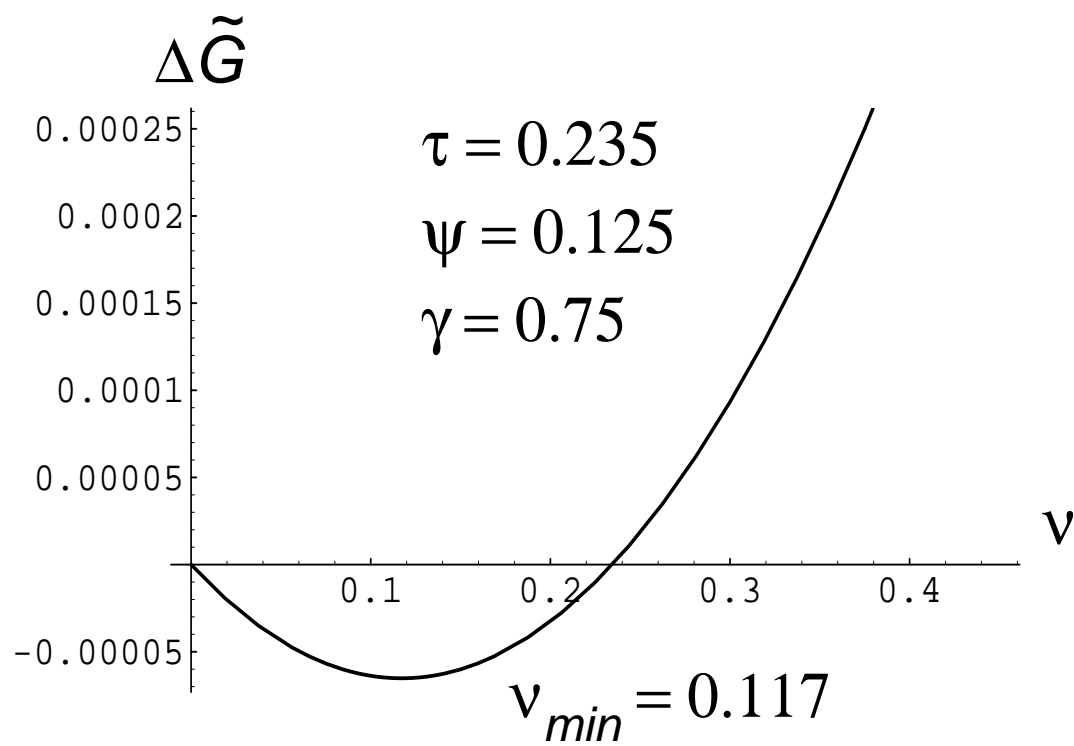FIG. 2. Free energy *vs* the phenomenological order parameter ζ.

FIG. 3. Dependence of $\Delta\tilde{\mathcal{G}}$ on the volume fraction of the new phase ν. Equilibrium ν for these τ, ψ and γ is 0.117.
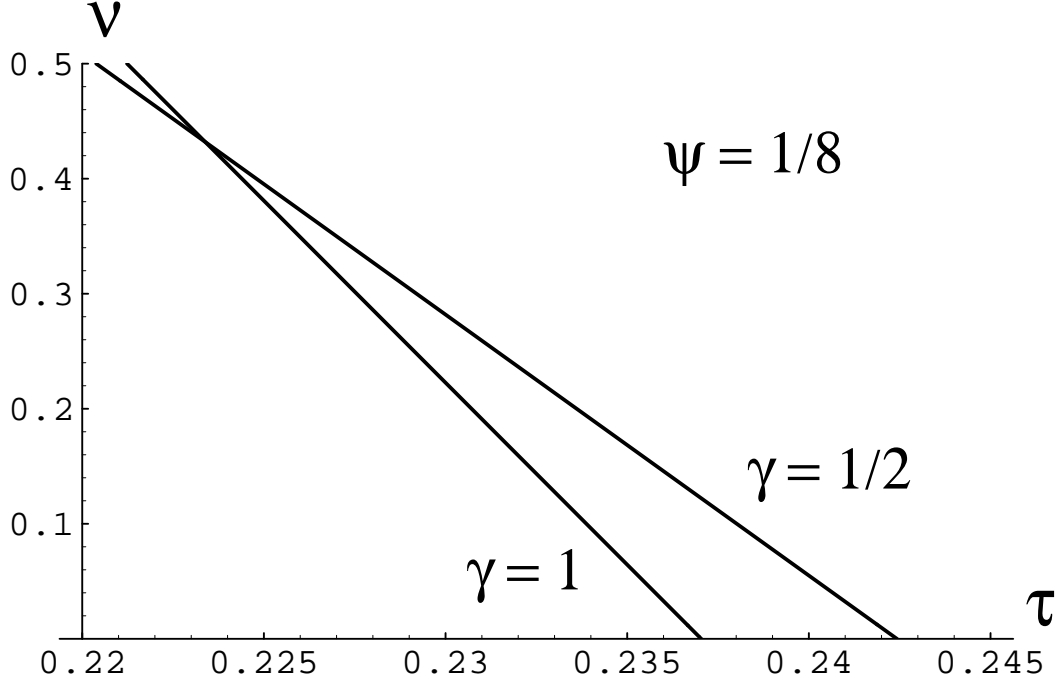

FIG. 4. Temperature dependence of the equilibrium volume fraction of the new phase ν for two different values of the ratio of elastic moduli γ.